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RESEARCH MEMORANDUM

THE PREPARATION, PHYSICAL PROPERTIES, AND HEATS OF
COMBUSTION OF FOUR ALKYL SILANES

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NATIONAL ADVISORY COMMITTEE
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COMBUSTION OF FOUR ALKYL-SILANES

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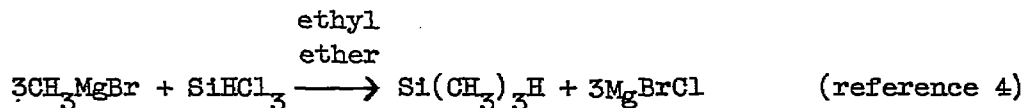
SUMMARY

A group of alkylsilanes consisting of monoethylsilane, diethylsilane, and trimethylsilane were prepared in 65- to 90-percent yield by reduction of the respective alkylchlorosilanes with either lithium hydride or lithium aluminum hydride. Tetramethylsilane was prepared by purification of commercial material. The boiling points, densities, refractive indices, and freezing points were determined and are presented together with a survey of literature values. The heats of combustion, obtained experimentally for the first time, are shown to be in good agreement with calculated values.

INTRODUCTION

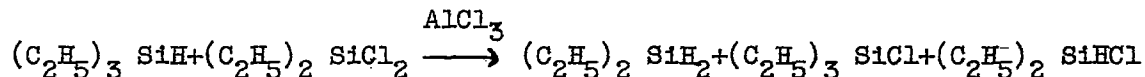
Recent reports from the NACA Lewis laboratory have shown that flame properties of a hydrocarbon fuel depend on the molecular structure (references 1 and 2). In order to extend this correlation to nonhydrocarbon fuels, a group of alkylsilanes consisting of monoethyl, diethyl, trimethyl, and tetramethyl silanes have been prepared.

Methods for the synthesis of alkylsilanes have been known for many years and the procedures developed are summarized in reference 3. The Grignard reaction, which is one of the most common methods, involves the reaction of a suitable alkyl magnesium halide with a halosilane in anhydrous ethyl ether:

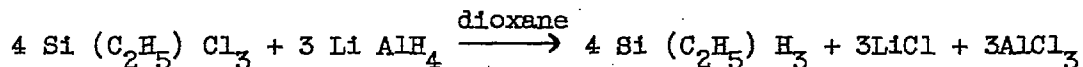


In the preparation of alkylsilanes, the Grignard reaction frequently gives a low yield of poor-quality product.

Diethylsilane can be prepared by a hydrogen - halogen exchange reaction (reference 5). If triethylsilane is treated with diethyl-dichlorosilane in the presence of anhydrous aluminum chloride, a 43-percent yield of diethylsilane is obtained along with considerable quantities of triethylchlorosilane and diethylchlorosilane:



A satisfactory method for preparing alkylsilanes from the corresponding alkylchlorosilanes was recently reported (reference 6). Lithium aluminum hydride or lithium hydride in anhydrous ethyl ether or dioxane readily replace chlorine atoms with hydrogen. This type of reaction is illustrated by the following equation for the preparation of monoethylsilane:



The reaction is rapid and yields of 80 percent or better are not uncommon. This method was chosen by the authors because it offered the most direct route to the desired compounds.

Few physical properties are available in the literature for compounds containing a Si-H bond and there are practically no thermodynamic data reported for these compounds. Measurements of freezing points of monoethylsilane, diethylsilane, and trimethylsilane; the density of diethylsilane at 0° C; and the heats of combustion for the four alkylsilanes are reported herein for the first time.

SYNTHESIS AND PURIFICATION

The method described in reference 6 was chosen in preference to the other available methods because it was expected to give a pure product in high yield. The alkylchlorosilanes were available from a commercial source and the chemical simplicity of this reaction made it fairly certain that the desired products could easily be obtained. No complicating side reactions, such as appear in the other methods outlined in the introduction, were likely.

The alkylsilanes were prepared by the reduction of the corresponding alkylchlorosilanes, as described in reference 6. The product was distilled from the reaction flask as formed and subsequently purified in a

3-foot vacuum-jacketed column. When traces of chloride were found in the fractionated material, they were removed by refluxing the alkylsilane over lithium hydride. The yield in each case was better than 65 percent, and in the preparation of monoethylsilane the yield was 90 percent.

The preparation of diethylsilane was undertaken first and lithium hydride, which was then available, was used as the reducing agent. Later experiments showed clearly that with lithium aluminum hydride the reaction was smoother and more complete. Therefore, in all subsequent reactions, lithium aluminum hydride was used as the reducing agent.

No modifications were made during the preparation of trimethylsilane, but in the synthesis of monoethylsilane a nitrogen atmosphere was used, which resulted in an improved yield. It is well known that the Si-H bond is easily oxidized and it is probable that at the various reaction temperatures (approximately 100° C) a portion of the alkylsilane formed is oxidized. The use of an inert atmosphere minimizes yield loss through oxidation.

Tetramethylsilane was purified by distillation over lithium hydride followed by percolation through a tube packed with silica gel.

MEASUREMENT OF PHYSICAL PROPERTIES

Time-temperature curves for the alkylsilanes, as shown in figure 1, were determined by the method of reference 7 and the freezing points were obtained by an analysis of these curves (reference 8). These values and all other available physical data are listed in table I (references 4, 5, 6, 9, 10, and 11). Tetramethylsilane is reported to have two crystalline modifications (reference 10). The conditions for obtaining each form were not ascertained in this investigation; the β form was more readily obtained. The values that were obtained showed substantial agreement with the reported values.

The refractive index values n_D^{20} reported in table I were determined with an Abbé refractometer.

Densities were measured with a fine-capillary Sprengel type pycnometer. The temperature was kept at 20° C \pm 0.02 during the course of the volume measurement. For those measurements made at 0° C, a clear glass Dewar flask containing a water-ice slush was used. By constant agitation, the temperature could be kept in the range 0° to 0.02° C. The densities of benzene at 20° C and of t-butyl benzene at 0° C were

determined with the pycnometer and also with a specific-gravity balance in order to check the accuracy of the method. The results showed that measurements at 20° C were accurate to ± 0.0002 gram per milliliter, whereas at 0° C the accuracy is not better than ± 0.0005 gram per milliliter. After determining the density of the alkylsilane with the pycnometer, another measurement was made with the specific-gravity balance. In all cases, the specific-gravity-balance values were higher than those determined with the pycnometer. The balance values are not reported because oxidation and hydrolysis can occur during the measurement and these values are of doubtful accuracy.

HEATS OF COMBUSTION

The heat of combustion is an important quantity in flame-speed theory and in calculating the expected performance of a fuel in an engine. Because this information was unavailable for the four alkylsilanes prepared, the heats of combustion were determined at the Lewis laboratory. The instrument available was a Parr Adiabatic Calorimeter equipped with a Parr Ilium constant-volume bomb. Inasmuch as these alkylsilanes have low boiling points, some method had to be devised whereby an accurate weighing of sample could be accomplished. In addition, it was expected that, should the material come in contact with oxygen under pressure before the ignition period, spontaneous ignition would occur and an accurate temperature rise could not be obtained, which proved to be the case, as will be shown later.

At first, thin soft-glass bulbs were made according to the directions of reference 12. These bulbs were difficult to fill completely and broke very frequently when the bomb was filled with oxygen under pressure. A new design, which consisted of a bulb made of soft glass connected to a short piece of 3-millimeter soft-glass tubing drawn out to a capillary, was adopted. The wall of the bulb was several times thicker than those described in reference 12, with a thickness of about 1 millimeter. The volume of the bulb was about 1 milliliter. The capillary was made wide enough so that a size 22 hypodermic needle could be inserted into the bulb. This design worked well for the alkylsilanes with higher boiling points but could not be used for monoethylsilane or trimethylsilane. These compounds had to be handled in a vacuum system and sealed in containers somewhat different in design, as discussed in the experimental section.

Several times incomplete combustion occurred due to improper filling of the enclosed volume of the bulb. In such cases, the bulbs did not explode but merely melted and material trapped inside did not completely burn.

In two cases, bulbs containing monoethylsilane exploded after the bomb had been filled with oxygen but before being placed in the calorimeter, and an immediate reaction occurred. When the bomb was opened, large amounts of silicon dioxide were found and, in general, the appearance of the bomb was identical with that noted after a normal combustion. There is therefore no doubt that monoethylsilane ignites spontaneously in pure oxygen. This evidence, coupled with the fact that the heat-of-combustion data were readily reproducible for the four alkylsilanes, indicates that spontaneous combustion in the presence of oxygen is a common property.

Using the method of reference 13, heats of combustion were calculated for each of the silanes from Pauling's table of bond energies. These values are in good agreement with those experimentally determined. All data relative to the heats of combustion are listed in table II.

EXPERIMENTAL

Synthesis and Purification

Monoethyltrichlorosilane and diethyldichlorosilane of 98-percent purity, and trimethylchlorosilane and tetramethylsilane of 99-percent purity were obtained from commercial sources. The purity was stated in the specifications received from the manufacturer.

The preparation of monoethylsilane is described in detail to illustrate the general procedure. The apparatus consisted of a 5-liter, three-necked flask fitted with a mineral-oil sealed Hershberg stirrer. The side necks were provided with openings for a flow of anhydrous nitrogen gas, a dropping funnel, a thermometer, and an eight-bulb condenser. A dry ice-acetone still head was mounted atop the bulb condenser and was fitted with a receiver packed in dry ice. All openings exposed to the atmosphere were protected with calcium-chloride drying tubes. About 1200 milliliters of freshly-distilled dioxane was placed in the flask along with 85 grams (2.23 moles) of lithium aluminum hydride, which had been pulverized in a dry box and suspended in 500 milliliters of dioxane. The system was flushed with dry nitrogen, stirred, and brought to reflux (100° - 105° C). After $1/2$ hour, the rate of stirring was decreased to 1 revolution per second and a constant nitrogen flow through the reaction flask was maintained. Three-hundred and twenty-eight grams (2.0 moles) of monoethyltrichlorosilane was added over a period of $8\frac{1}{2}$ hours and the product was distilled from the mixture as formed. This procedure was followed by 2 hours of vigorous stirring to drive all the product from the reaction mixture. A

total of 115.5 grams of impure monoethylsilane was obtained and this material was then distilled in a 3-foot vacuum-jacketed column packed with glass helices. The material, which distilled in the range -12.5° to -10.5° C, was collected and amounted to 105.6 grams (88 percent based on monoethyltrichlorosilane). A Beilstein test showed that traces of chloride were present, but these traces were removed by distillation over lithium hydride.

Trimethylsilane and diethylsilane were prepared in a similar manner with the exception that a nitrogen atmosphere was not employed. Yields of 70 to 80 percent for the trimethylsilane and 65 to 75 percent for the diethylsilane were realized. Lithium hydride was the reducing agent in the preparation of diethylsilane.

Tetramethylsilane was not synthesized, but purchased and purified. Distillation over lithium hydride in a 5-foot vacuum-jacketed glass-helix packed column removed all traces of chloride but other impurities were present, as judged by the freezing curve. Passing the material through silica gel, however, gave a pure product.

Measurement of Heats of Combustion

The boiling points of diethylsilane and tetramethylsilane were sufficiently high that these compounds could be handled in the soft-glass bulbs previously described. The procedure in making a determination was to weigh the bulb assembly empty, then fill it with liquid from a hypodermic syringe up to the capillary. The bulb was immersed in powdered dry ice, the top part flushed with dry nitrogen, and the bulb immediately sealed off at the capillary. Both bulb and extra glass were then weighed to provide the weight of the alkylsilane used. The bomb was assembled and the bulb placed in the sample cup and attached to the ignition wire, which had been shaped to give a circle of wire at the bottom, with a weighed piece of cellophane adhesive tape of known heat of combustion. Best results were obtained when the wire loop was attached to the bulb area rather than to the stem. If the bulb had been correctly filled, it did not break until current was passed through the ignition wire, which caused the liquid to expand and break out of its glass container.

Because monoethylsilane and diethylsilane have boiling points much below room temperature, they could not be introduced into a bulb from a hypodermic syringe. They could be filled, however, from a high vacuum system. Approximately the same design bulb was used except that it was made of pyrex glass rather than soft glass. For the bulb to break

properly it had to be filled with just enough liquid to occupy the entire volume at room temperature. In order to accomplish this, the bulbs were attached to a piece of 1-millimeter capillary tubing, which was connected to the vacuum system through a stopcock and standard taper joint. The bulbs were filled with liquid in the vacuum system, then the stopcock was closed and the liquid was allowed to heat up to room temperature. Excess liquid was removed by manipulation of the stopcock until the liquid level ended about 1 inch above the joint between the capillary tubing and the bulb. The liquid was then quickly frozen and the tube was sealed off at this point of junction. Both bulb and residual glass were weighed and the weight of liquid was determined. Ignition in the bomb was carried out exactly as before, except that prior to closing the bomb the bulb was cooled down by touching it with a piece of dry ice.

The determination of the heat of combustion of monoethylsilane was complicated by the presence of an orange-tan solid among the combustion products. This solid indicated incomplete combustion, a conclusion that was supported by the fact that the experimental values were consistently below the calculated values. This difficulty was removed by using a sample holder $1\frac{1}{2}$ inches high in place of the ordinary 1/2-inch holder.

Analyses for carbon and silicon were made on the products of combustion in some experiments to check the completeness of combustion. The carbon dioxide was determined by passing the gaseous products of combustions through a Nesbitt absorption bulb filled with Ascarite and Anhydrone after first drying the gas by passage through Anhydrone. The bomb was flushed several times with oxygen to remove all the combustion gases. A correction term for the carbon dioxide formed by combustion of the cellophane tape was included, and it was assumed that the amount of carbon dioxide left in the moisture in the bomb was negligible due to the presence of nitric acid in this moisture. Silicon dioxide was determined by carefully removing the contents of the bomb, leaching out the iron oxide (formed by ignition of the wire) with dilute hydrochloric acid, and then igniting to constant weight. These analyses indicate that the combustion proceeds to at least 98 percent of completion. The results are included in table II.

CONCLUDING REMARKS

Monoethylsilane, diethylsilane, and trimethylsilane were prepared in 65- to 90-percent yield from their respective alkylchlorosilanes. In

addition, tetramethylsilane was purchased and purified. A number of physical properties were measured, some for the first time, including freezing points, a density at 0° C, and heats of combustion.

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TABLE I - PHYSICAL PROPERTIES OF ALKYL SILANES

Compound	Freezing point (°C)	Boiling point (°C)	Density (grams/ml)	Index of refraction (n_D^{20})
Monoethylsilane	-179.7 ^a	-14.5 ^a		
Diethylsilane	-134.39 ^a	-14 ^b	20° = 0.6832 ^{a, b}	1.3920 ^a
		55.79 (755 mm) ^a	20° = 0.6843 ^c	1.3918 ^b
		55.99 (760 mm) ^a		1.3921 ^c
		54 ^b	0° = 0.7026 ^a	
Trimethylsilane	-135.89 ^a	56 ^c		
		9 ^a		
		9-11 ^d		
Tetramethylsilane	$\alpha = -101.70$ } ^a	27 ^a	20° = 0.6388 ^a	1.3582 ^a
	$\beta = -99.50$ } ^f	26-27 (760.7 mm) ^e	0°/4 = 0.6688 } ^e	1.3587 ^g
	$\alpha = -102.12$ }	26.64 ^f	10°/4 = 0.6578 }	
	$\beta = -99.04$ }	26 ^g	17°/4 = 0.6497 }	
			21.9°/4 = 0.6445 }	

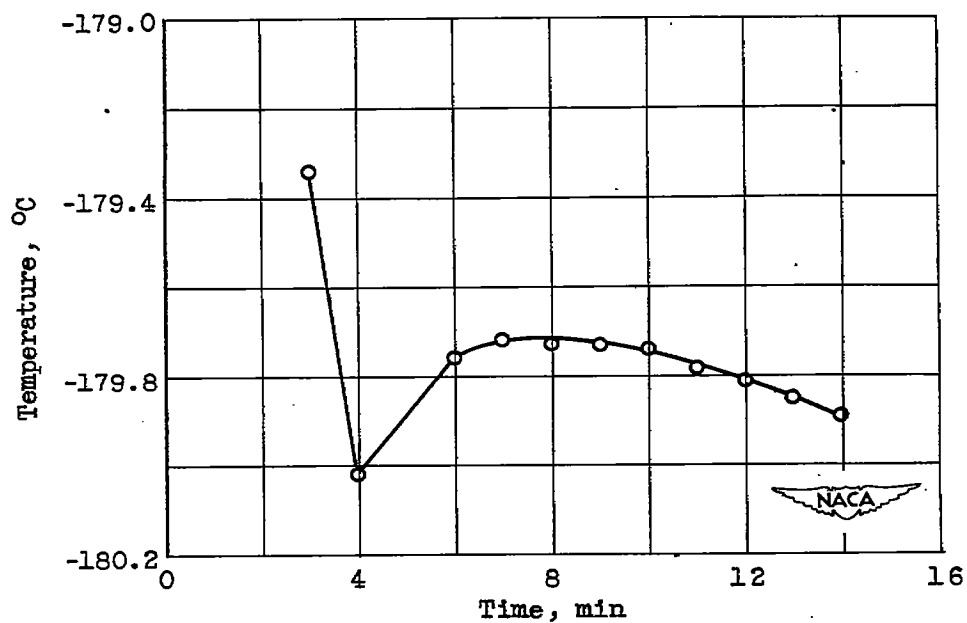
^aPresent report.^bReference 6.^cReference 5.^dReference 4.^eReference 9 (These are specific gravities).^fReference 10.^gReference 11.

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TABLE II - ANALYSES AND HEATS OF COMBUSTION OF ALKYL SILANES

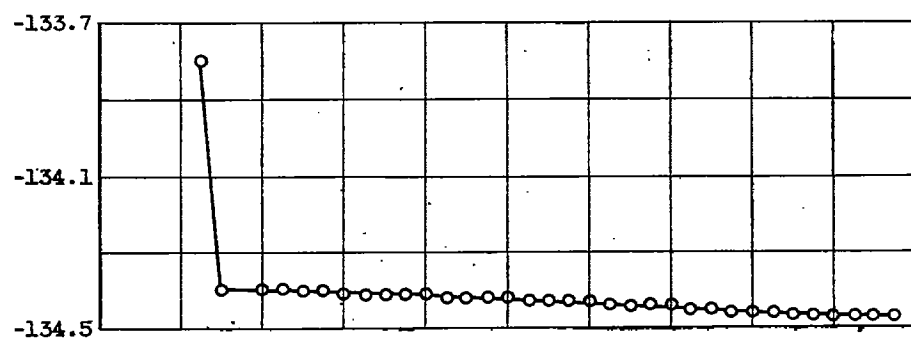
Compound	Analyses, (percent)				Heat of combustion (kcal/gram)		
	Carbon		Silicon				
	Calculated	Found	Calculated	Found	Calculated	Found	
					Gross ^a	Gross	Net
Monoethylsilane	39.94	39.68	-----	-----	10.59	10.85	10.15
Diethylsilane	54.47	53.84	31.82	31.21	10.57	10.82	10.11
Trimethylsilane	48.58	47.42	-----	-----	10.25	10.37	9.66
Tetramethylsilane	54.47	53.81	31.82	30.92	10.32	10.46	9.75

^aCalculated from Pauling's table of bond energies, as shown in reference 13.

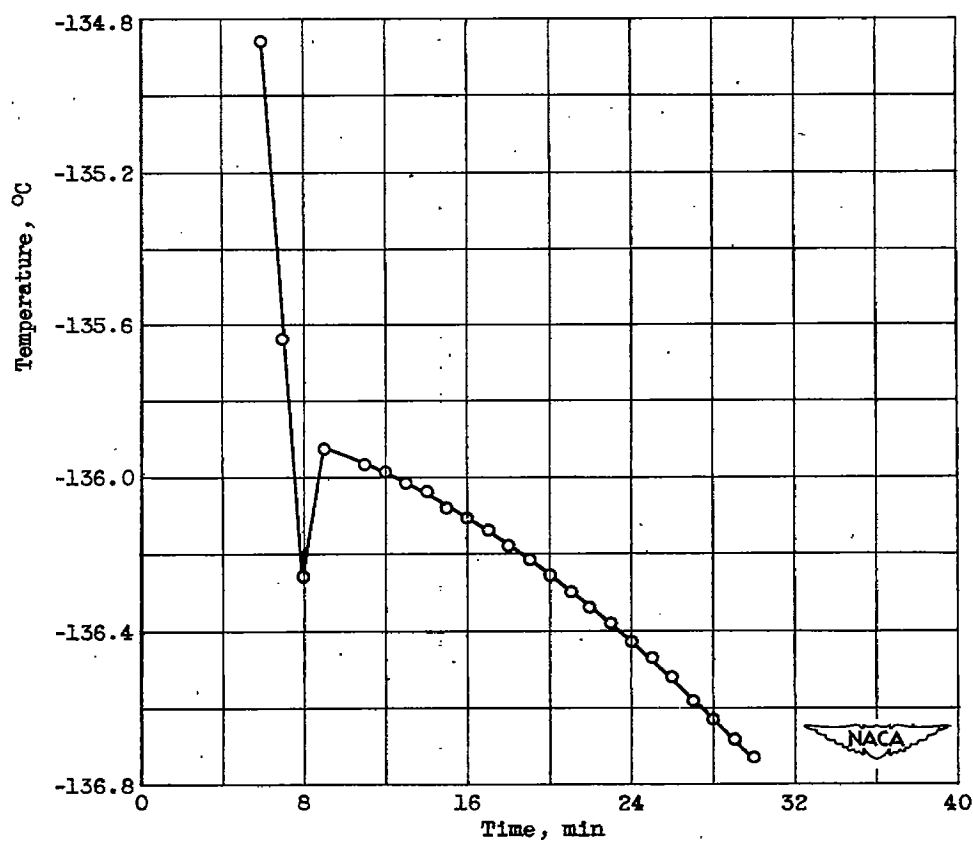


(a) Monoethylsilane.

Figure 1. - Time-temperature freezing curves for alkylsilanes.



(b) Diethylsilane.



(c) Trimethylsilane.

Figure 1. - Continued. Time-temperature freezing curves for alkylsilanes.

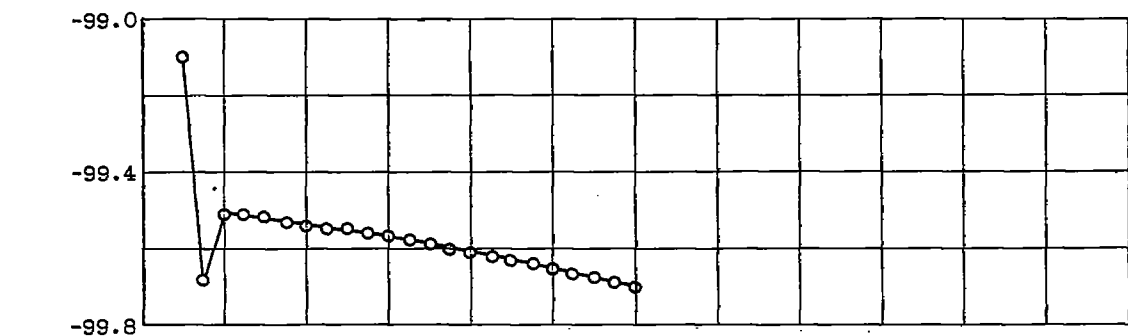
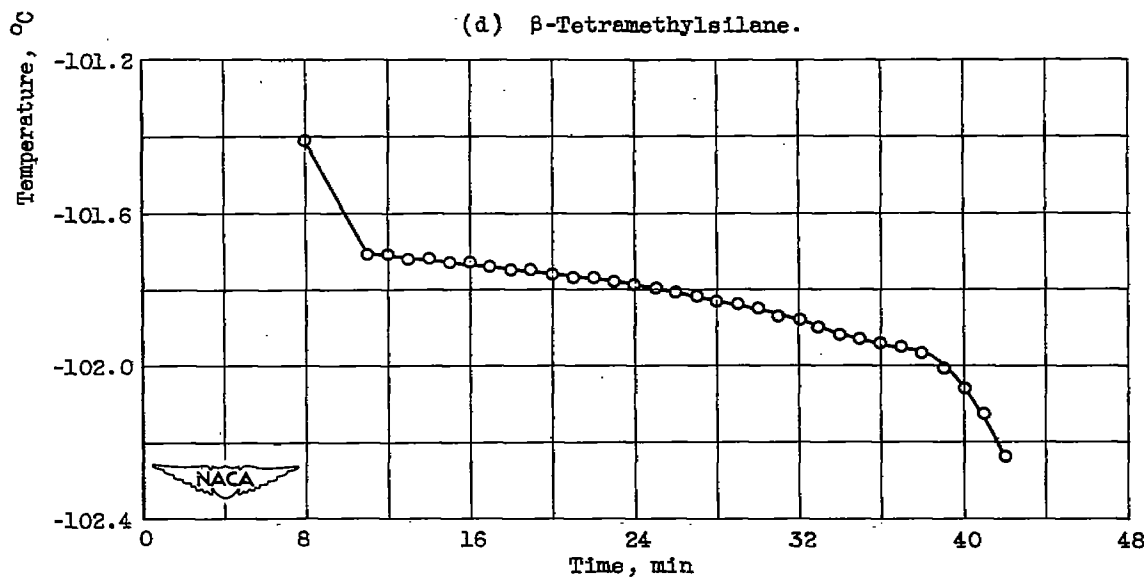
(d) β -Tetramethylsilane.(e) α -Tetramethylsilane.

Figure 1. - Concluded. Time-temperature freezing curves for alkylsilanes.

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